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54 Cationic polyelectrolytes and their production.

57 Improved performance and physical properties are obtainable from acrylamide-dialkylaminoalkyl acrylate polymers when the polymers are made by using a blend of dialkylaminoalkyl acrylate acid addition or quaternary ammonium salt with dialkylaminoalkyl methacrylate acid addition or quaternary ammonium salt.

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CATIONIC POLYELECTROLYTES AND THEIR PRODUCTION

Cationic polyelectrolytes that are high molecular weight water soluble copolymers of acrylamide with a cationic ester are well known for use as, for instance, flocculants, aqueous thickeners and retention aids in paper manufacture.

Most literature disclosures of such copolymers mention that the comonomer can be quaternised or salified dialkylaminoalkyl acrylate or dialkylaminoalkyl methacrylate and such disclosures are then generally exemplified by copolymers of acrylamide with quaternised or salified dialkylaminoalkyl methacrylate. Such copolymers have been widely used commercially. Certain copolymers of acrylamide with quaternised or salified dialkylaminoalkyl acrylate have also been used.

In US Patent Specification No. 4319013 and 4396752 powdered copolymers of acrylamide with quaternised or salified dimethylaminoethyl acrylate are described. It is stated that the described copolymers have the cationic units spaced regularly along the chain, and that this is the result of the reactivity ratios r_1 and r_2 for the monomer pairs from which the copolymers are obtained. Accordingly the use of the acrylate comonomer, rather than the methacrylate comonomer, is stated to give a more regular distribution of cationic units.

It is stated that the defined copolymers of acrylamide and dimethylaminoethyl acrylate have a very distinct superiority as flocculants compared to copolymers of dimethylaminoethyl methacrylate.

The present position therefore is that acrylamide copolymers with cationic methacrylate as the sole comonomer are widely described and used, acrylamide copolymers with cationic acrylate as the sole comonomer have been widely used, and the quoted literature states

clearly that powdered copolymers with cationic acrylate are better than the powdered copolymers with cationic methacrylate, and advances theoretical reasons associated with reaction rates of the various monomers for this.

5 Despite the different reaction rates of the cationic methacrylate ester monomer and the cationic acrylate ester monomer and despite the statements in the literature we have now surprisingly found that improved properties are obtained if the polymer is a terpolymer of
10 acrylamide with both acrylate and methacrylate cationic units.

Novel cationic polyelectrolytes are terpolymers of (a) dialkylaminoalkyl acrylate, (b) dialkylaminoalkyl methacrylate and (c) acrylamide and are in the form of
15 acid addition or quaternary ammonium salts.

These novel terpolymers can be made by conventional polymerisation techniques on the monomers while in free base form followed by conversion to the acid addition or quaternary ammonium salt after polymerisation but
20 preferably are made by polymerisation in aqueous solution of the monomers in salt form.

A process according to the invention for making improved cationic polyelectrolytes comprises polymerising a blend of (a) dialkylaminoalkyl acrylate as acid
25 addition or quaternary ammonium salt, (b) dialkylaminoalkyl methacrylate as acid addition or quaternary ammonium salt and (c) acrylamide whilst in aqueous solution to form an aqueous gel, and then if desired drying the resultant gel, preferably to form a
30 powder. Thus even though the reaction rates during this process would, according to U.S. 4,319,013, give a non-random polymer in fact we find the resultant terpolymer has great advantages compared to the comonomers that have previously been described and used.

One advantage obtainable by the invention is that a terpolymer is, in general, more effective (at a given molecular weight) as a flocculant than either corresponding copolymer. By the invention it is possible, under otherwise similar polymerisation conditions, generally to obtain an increased molecular weight, especially compared to the comonomer of a and c. The polymers are preferably made by bead polymerisation and the invention then has the great advantage that the blends of cationic monomers, even when one monomer is present in a small amount, results in the production of beads having less irregularity in shape and/or size, especially compared to the copolymers of a and c.

Within this specification we use the term copolymer to refer to polymers made from two monomer types, a and c or b and c, and the term terpolymer to describe copolymers made from three monomer types a, b and c. These terpolymers are generally formed from only the three specified types of monomer and generally are formed from acrylamide and one methacrylate and one acrylate monomer. However, if desired, blends of the methacrylate (type b) or of the acrylate (type a) may be used and in some instances an additional type of comonomer can be included in small amounts, for instance up to 10 % based on total copolymer, provided such additional comonomer or monomers does not detrimentally affect the properties of the product. Such other comonomers can be cationic but are generally non-ionic and will preferably be monoethylenically unsaturated monomers.

In each of the monomers a and b the alkyl groups carried by the amino group preferably contain 1 to 4 carbon atoms and most preferably are methyl or ethyl. Generally both alkyl groups are the same. The alkylene group preferably contains 2 to 4 carbon atoms and most preferably is ethylene. Any of these groups may be

substituted, for instance by hydroxyl. The preferred monomers are diethylaminoethyl acrylate or methacrylate or, in particular, dimethylaminoethyl acrylate or methacrylate.

5 The acid addition salt or quaternary ammonium salt can be provided by any of the conventional salt-forming groups. For instance an acid addition salt can be formed with hydrochloric acid or other inorganic acid whilst a quaternary addition salt can be formed with
10 dimethyl sulphate or methyl chloride or other quaternising compounds.

It is generally preferred for the polymers to be made as powders, since the powdered ter polymers appear to exhibit greater general improvement in flocculation
15 performance over the corresponding copolymers than exists when the terpolymers and copolymers are in liquid form.

The production of powdered terpolymers can be conducted whilst the aqueous solution is in bulk, i.e., as a conventional aqueous gel polymerisation, followed by
20 comminution and drying of the resultant gel mass to form the desired powder. For instance the polymerisation may be conducted to form a stiff gel which may then be comminuted to large particles which may then be dried, further comminuted and further dried, all in conventional
25 manner.

Preferably however the production of powdered terpolymers is conducted as a reverse phase bead polymerisation process. Thus the polymerisation is conducted whilst the aqueous solution of monomers is
30 dispersed in a water immiscible liquid. This results in the production of a dispersion of gel particles in the liquid and this dispersion is dried, for instance as a result of azeotropic distillation, and the particles are separated from the dispersion, for instance by

centrifuging or filtering. The separated particles may be further dried.

Reverse phase bead polymerisation processes are well known for instance from US Patent No 2982749. Typically, the aqueous monomer solution is stirred into the non-aqueous liquid in the presence of a polymeric stabiliser to form aqueous monomer beads of the desired size, and polymerisation is then initiated. The size of the resultant polymer particles, when dry, is preferably dictated by the size of the dispersed aqueous monomer particles and this in turn is affected by the conditions under which the particles are formed, and in particular by the amount of shear that is applied and by the presence or absence of a surfactant. Surfactant may be used, for instance as in U.S.P 4,319,013 in order to obtain smaller particles but if larger particles are desired then it can usually be omitted.

Suitable polymeric stabilisers, water immiscible liquids and other polymerisation conditions are described in the literature, for instance in European patent specification 0126528.

The process conditions used in the invention are generally such that the dry particles have a size of at least 10 microns and usually at least 50, and preferably at least 100, microns. The maximum size is generally below 3 mm with preferred products consisting mainly of particles in the range 200 microns to 1 mm, or sometimes up to 2 mm.

The terpolymer beads obtained in the invention can have a more regular shape and/or size than the corresponding copolymer beads, especially compared to copolymers of a and c. Thus a difficulty with the known processes is that there is a tendency for the beads to have an irregular shape and/or an irregular particle size. The ideal product would consist of substantially

spherical beads having a narrow range of particle sizes. Unfortunately, we have found that when a copolymer of acrylamide and dialkylaminoalkyl acrylate is formed by conventional reverse phase bead polymerisation there is a particularly marked tendency for the beads to be of irregular shape and/or irregular size, and in particular there can be a significant proportion of dusting.

We have surprisingly found that the replacement of some of the cationic acrylate ester by cationic methacrylate ester reduces this tendency to dusting and improves the regularity of bead shape or bead size or both. There is generally no advantage in using more than 25% methacrylate, based on the molar amount of acrylate and methacrylate ester, and satisfactory improvement is generally obtained with from 5 to 15% methacrylate.

If a liquid grade of terpolymer is required it is preferably produced by polymerising the aqueous solution while dispersed in a water immiscible liquid to produce a stable dispersion of aqueous polymer gel particles in the water immiscible liquid, i.e. by a reverse phase suspension or emulsion polymerisation process conducted to give a very small particle size, e.g. 0.1 to 3 microns. Such processes are described in, e.g. EP 0126528. The dispersion may be dried by azeotropic distillation to give a dispersion of dry polymer particles in water immiscible liquid.

All processes used in the invention generally require polymerisation of a solution containing 20 to 60%, generally 25 to 40%, by weight monomer, in the presence of an initiator (usually redox or thermal) until the polymerisation terminates. The temperature generally starts low, e.g. 0 to 30°C but may rise to, e.g. 40 to 95°C.

The molar proportion of acrylamide, based on the molar amount of acrylamide, dialkylaminoalkyl acrylate

and dialkylaminoalkyl methacrylate, is generally from 99 to 20%. Preferably, the amount of acrylamide is at least 50%, often at least 60%. Often it is below 95%. All percentages herein are molar, unless otherwise specified.

5 The ratio of monomer a:monomer b used in the process of the invention, and thus the ratio of groups a and b in the final polymer, may on a molar basis range from 99:1 to 1:99 but best performance is generally obtained in the range 88:12 to 5:95, preferably 85:15 to 15:85 and most
10 preferably 80:20 to 20:80.

 In one class of processes the ratio is 1:99 to 50:50, i.e., the cationic monomer is mainly methacrylate. In these processes the ratio is generally 40:60 to 5:95 with best results generally being achieved in the range 25:75
15 to 5:95. For instance replacement of 8 to 22%, preferably 10 to 20% of the methacrylate by acrylate gives a significant improvement in flocculation performance properties and very good results are obtained when the ratio is below 12:88, preferably below 15:85.

20 In another class of processes the ratio a:b is from 50:50 to 95:5, the cationic monomers being mainly acrylate. Preferably the ratio a:b is 60:40 to 95:5, most preferably 75:25 to 95:5. The replacement of, for instance, 8 to 22%, preferably 10, 12 or 15% up to 20%
25 can lead to improved flocculation performance properties and to increased molecular weight, as well as to improved bead size and shape and very good results are obtained when the ratio is below 88:12, preferably below 85:15..

 Although the invention is of particular value when up
30 to 25%, for instance up to 20 or 22%, of type a or type b monomer is to be replaced by type b or type a monomer respectively valuable performance results are also obtainable when the ratio a:b is in the range 70:30 to 30:70, most preferably 40:60 to 60:40.

The polymerisation is preferably conducted under known conditions such that the polymers are water soluble and have a high molecular weight, generally above 1 million, for instance up to 30 million. The intrinsic viscosity, measured in molar sodium chloride solution at 25°C, is generally above 6, for instance from 8 to 14.

Although the polymers can be used for any of the purposes for which such high molecular weight cationic polyelectrolytes are suitable, the invention is of particular value when applied to the production of flocculants and so the invention includes also processes in which aqueous dispersions are flocculated by adding to the dispersion, in known manner, one of the flocculants produced in accordance with the invention.

The following are some examples.

EXAMPLE 1

An aqueous solution of 10 % methyl chloride quaternised dimethylaminoethyl acrylate and 90 % acrylamide was prepared having a pH of around 4 and was dispersed in a non-aqueous liquid consisting of a blend of solvent 41 (95% by weight) and per chlorethylene (5% by weight) in the presence of 0.2% by weight of a suitable amphipathic polymeric stabiliser, for instance a stabiliser as described in British Patent No.1482515 or US Patent No. 4158726. The dispersion of the aqueous solution into the non-aqueous liquid was conducted by conventional stirring equipment with sufficient agitation to give beads about 0.75 mm in diameter. Polymerisation was then initiated in conventional manner using various amounts of potassium bromate and sulphur dioxide. The reverse phase bead polymerisation was allowed to go to completion in conventional manner, the water was removed by azeotroping the resultant product and the substantially dry beads were then separated from the non-aqueous liquid by centrifuging.

When this process was carried out using 12 ppm potassium bromate and 21 ppm sulphur dioxide the temperature rise after 5 minutes was 13°C, the final intrinsic viscosity was 6.4 dl/g and the viscosity of a 1% by weight solution of the polymer (measured by SLV No. 3 at 25°C) was 1910. Any reduction in the amount of initiator resulted in a coagulated mixture.

When the process was conducted under identical conditions except that 10% of the acrylate units were replaced by methyl chloride quaternised dimethylaminoethyl methacrylate units the temperature change after 5 minutes was 9°C, the final intrinsic viscosity 8.4 dl/g and the 1% solution viscosity 2291. Using the same blend of monomers, the amount of initiator could be reduced significantly without coagulation and at 9 ppm potassium bromate and 15.8 ppm sulphur dioxide the temperature rise after 5 minutes was only 3°C, the final intrinsic viscosity was 12.6 dl/g and the 1% by weight solution viscosity was 3473.

Analysis of the products showed that the copolymer with acrylate alone contained a significant proportion of mis-shapen beads and of fines, while each of the terpolymers had a more regular particle shape and fewer fines. Thus each of the products were sieved to separate fines (1 to 75 microns) from the beads (75 to 810 microns). The proportion of fines in the copolymer was 5 to 10% by weight but the proportion in the terpolymers was below 3% by weight.

EXAMPLE 2

A copolymer of 86 % acrylamide and 14 % of the quaternised acrylate, and terpolymers in which 10 and 20% respectively of the acrylate was replaced by the corresponding methacrylate, were prepared by the general method and using the same monomers as in Example 1. It was observed that the inclusion of 10% of the

methacrylate improved the flocculation performance of the copolymer and the inclusion of 20% of the methacrylate improved it still further.

EXAMPLE 3

- 5 A copolymer of 87 % acrylamide and 13 % methyl chloride quaternised dimethylaminoethyl methacrylate was formed, as was a terpolymer in which 10 mole % of the methacrylate was replaced by acrylate, using the general method shown in Example 1. The flocculation performance
10 of the resultant products was observed. None were as effective as the products of Example 2 but it was observed that the terpolymer was much more effective than the copolymer.

EXAMPLE 4

- 15 A range of copolymers were prepared by reverse phase bead suspension polymerisation as described in Example 1 using 62 mole percent acrylamide and 38 mole percent cationic monomers. The cationic monomers were the methyl chloride quaternary salt of dimethylaminoethyl
20 acrylate (A) and the methyl chloride quaternary ammonium salt of dimethylaminoethyl methacrylate (M).

- Each preparation was evaluated as a dewatering acid using a digested sewage sludge, to which 0.3 moles of sodium chloride had been added, as test substrate.
25 Dewaterability was measured in terms of CST (capillary suction time).

- From CST values obtained at each of two dose levels a performance index, relative to the performance of the copolymer prepared from 100% A was calculated for each
30 preparation.

Where the CST using the 100% A preparation is X and that obtained for the other preparation is Y:-

$$\text{Performance Index} = \frac{(X - Y)}{X} \cdot 100$$

- Preparations were grouped according to cationic
35 monomer/mixed cationic monomer with there being between 1

and 10 preparations within each group. The average intrinsic viscosity (IV) in dl/g and performance index (PI) was calculated for each group. Performance index was then corrected for variation in molecular weight by multiplying each value by a ratio of highest IV:IV of preparation under consideration. Results were as follows:-

	<u>Ratio of A:B</u>	<u>Average IV</u>	<u>PI</u>	<u>Corrected PI</u>
	100: 0	6.7	0	0
10	89: 11	7.3	13	16
	74: 26	8.1	40	43
	48: 52	8.0	39	42
	38: 62	7.5	41	48
	29: 71	6.4	17	23
15	24: 76	8.7	40	40
	19: 81	6.9	29	36
	0:100	7.2	-11	-10

EXAMPLE 5

- 20 A range of copolymers was prepared by gel polymerisation using 93 mole % acrylamide and 7 mole % cationic monomers. The cationic monomers were as described in Example 4 and designated A and B. The gel polymerisation was conducted on a 29% solution in water
- 25 of the monomer blend in the presence of 10 ppm potassium bromate, 25 ppm sodium sulphate and 100 ppm azdn. The reaction was initiated at 0°C and the temperature rose to 92°C before the reaction terminated. The gel was cooled, minced, dried at 40°C and ground to powder.
- 30 Each preparation was evaluated as a dewatering aid for sewage sludge, to which 0.3 moles of sodium chloride had been added. Performance indices and corrected performances indices were obtained and calculated as described in Example 4, whilst using the first product of
- 35 this series of single products as reference.

	<u>Ratio of A:B</u>	<u>I.V.</u>	<u>P.I.</u>	<u>Corrected P.I.</u>
	0:100	5.3	0	0
	9.4: 90.6	5.8	10	18
	23.7: 76.3	8.7	29	35
5	48.3: 51.7	9.3	29	32
	73.7: 26.3	10.3	34	34
	89.4: 10.6	10.4	41	41
	100: 0	9.9	28	29

EXAMPLE 6

10 Two copolymers of 78.5 mole % acrylamide and 21.5 mole % cationic monomers, were prepared, by reverse phase polymerisation followed by azeotropic distillation, at similar I.V. The cationic monomers were as described in Example 4 and designated A and B. The polymerisation

15 conditions were similar to those described in Example 1 except that sufficient sorbitan mono-oleate was added to give a stable dispersion, after drying, of particles mainly below 2 microns in size dispersed in oil.

Each preparation was evaluated on sewage sludge to which 0.5 moles of sodium chloride had been added. A performance index was calculated as described in Example 4 using the product prepared from 100 mole % dimethylaminoethyl acrylate methyl chloride quaternary salt as the reference

25	<u>Ratio A:B</u>	<u>I.V.</u>	<u>P.I.</u>
	100: 0	6.7	0
	89.4:10.6	7.0	20

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CLAIMS

1. A high molecular weight cationic polyelectrolyte formed from acrylamide and cationic monomer characterised in that the polymer is a terpolymer of (a) dialkyl-
5 aminoalkyl acrylate acid addition or quaternary ammonium salt with (b) dialkylaminoalkyl methacrylate acid addition or quaternary ammonium salt and (c) acrylamide.
2. A polymer according to claim 1 in which the molar ratio a:b is 88:12 to 5:95, preferably 85:15 to 15:85,
10 and the amount of c is preferably 20 to 99%, most preferably 50 to 90%, molar.
3. A polymer according to claim 1 in which the ratio a:b is 80:20 to 20:80.
4. A polymer according to claims 1 in which the molar
15 ratio a:b is 60:40 (preferably 75:25) to 85:15.
5. A polymer according to any of claims 1 to 4 in which monomer a is dialkylaminoethyl acrylate acid addition or quaternary ammonium salt and monomer b is dialkylamino-ethyl methacrylate acid addition or quaternary ammonium
20 salt, wherein the alkyl groups are preferably methyl and the salt is preferably the methyl chloride or dimethyl sulphate quaternary ammonium salt.
6. A polymer according to any preceding claim which is a flocculant and has intrinsic viscosity greater than 6.
- 25 7. A polymer according to any preceding claim in the form of a powder, preferably beads.
8. A process of making high molecular weight cationic polyelectrolyte by polymerising acrylamide with cationic monomer characterised in that the process comprises
30 polymerising a blend of (a) dialkylaminoalkyl acrylate acid addition or quaternary ammonium salt, (b) dialkylaminoalkyl methacrylate acid addition or quaternary ammonium salt and (c) acrylamide while in aqueous solution to form an aqueous gel.

9. A process according to claim 8 in which the polymerisation is conducted while the aqueous solution is dispersed as beads in a water immiscible liquid and the resultant dispersion of gel beads is dried and the beads are separated from the dispersion.
10. A process according to claim 8 or claim 9 in which the molar ratio a:b is 88:12 to 5:95, preferably 85:15 to 15:85 and the amount of c is preferably 20 to 99%, most preferably 50 to 90%, molar.
11. A process according to of claims 8 to 11 in which the molar ratio a:b is 80:20 to 20:80.
12. A process according to any of claims 8 to 10 in which the molar ratio a:b is 60:40 (preferably 75:25) to 85:15.
13. A process according to any of claims 8 to 12 in which monomer a is dialkylaminoethyl acrylate acid addition or quaternary ammonium salt and monomer b is dialkylamino ethyl methacrylate acid addition or quaternary ammonium salt, wherein the alkyl groups are preferably methyl and the salt is preferably the methyl chloride or dimethyl sulphate quaternary ammonium salt.
14. A process according to any of claims 8 to 13 in which the polymer is a flocculant and has IV greater than 6.

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